slowly. The ether solution was separated, dried, and concentrated to yield 2.57 g of yellow oil. Heating the oil to 100° under reduced pressure (35 mm) removed 0.80 g of *n*-butyl bromide. The residual oil, which solidified on standing, was dissolved in 5 ml of pentane and cooled to $-18°$ for 3 hr. Filtration gave white needles of diphenylacetylene (61.5%), mp 57–58°.

Vapor phase chromatography (2-ft GE-SE-30; 190°) showed that the crude product contained by weight 59% diphenylacetylene, 3.3% of *trans*-α-*n*-butylstilbene, 1.2% starting material, 28.4% *n*-butyl bromide, 5.3% *n*-octane, and 3.4% *n*-butyl alcohol. This corresponds to an over-all yield of 89.3% diphenylacetylene, 3.8% *trans*-α-*n*-butylstilbene, and 1.2% *o*-bromodiphenylacetylene.

Registry No.—Diphenylacetylene, 501-65-5; *cis* **3**, 16897-91-9; *trans* **3**, 16915-88-1; *cis* **4**, 16897-92-0; *trans* **4**, 16915-89-2; *cis* **5**, 16897-93-1; *trans* **5**, 16897-94-2; **6a**, 16897-95-3; **6b**, 16897-96-4; α-(*o*-bromophenyl)acetophenone, 16897-97-5; 2,4-dinitrophenylhydrazone of α-(*o*-bromophenyl)acetophenone, 16915-90-5; deuterated diphenylacetylene, 16897-98-6.

Small-Ring Epoxides. II. 2,2,6,6,7,7-Hexamethyl-1,5-dioxadispiro[2.0.2.1]heptane[1a]

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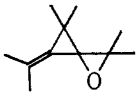
Contribution No. 1595 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401

Received March 7, 1968

2,2,6,6,7,7-Hexamethyl-1,5-dioxadispiro[2.0.2.1]heptane (**3**) has been prepared by epoxidation of its dimethylenecyclopropane precursor **2**. Thermolysis of the diepoxide gives two ketones, 2,2,5,5,6,6-hexamethyl-4-oxo-1-oxaspirohexane (**5**) and a compound tentatively assigned as 3,5,5-trimethyl-2-(1-hydroxy-1-methylethyl)cyclopent-2-enone (**6**). Acid-catalyzed rearrangement yields 2,2,4,4,5,5-hexamethylcyclopentane-1,3-dione (**14**) and 3,3,4,4,5,5-hexamethylcyclopentane-1,2-dione (**15**), probably by way of **5** as an intermediate. The rearrangement of **3** with diethylamide produces 2,5-dimethyl-4-isopropylidene-5-hydroxyhex-2-en-3-one (**17**). The mechanistic details of these transformations are discussed.

We have recently reported on the preparation and some of the reactions of the interesting oxaspiropentane derivative **1**.[2] Reaction of the precursor dimethylenecyclopropane **2** with an excess of peracetic acid leads, as expected, to the diepoxidation product, 2,2,6,6,7,7-hexamethyl-1,5-dioxadispiro[2.0.2.1]heptane (**3**), in good yield. The present paper is concerned with some of the properties of diepoxide **3**.

The assignment of the *anti* structure **3** as opposed to *syn* structure **4** is based on a 100-MHz spectrum of the homogeneous epoxidation product which shows three equivalent sharp methyl peaks rather than the four types of methyls expected for **4**. The predominance of epoxide **3** can probably be attributed to unfavorable dipole–dipole interactions in the transitions state leading to the *syn* diepoxide.[3]



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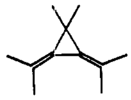

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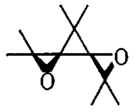

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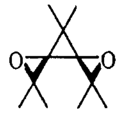

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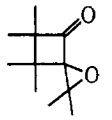
Pyrolysis of **3** in a vacuum pyrolysis system at 400° gave two major compounds. The predominant product (75%) was identified as 2,2,5,5,6,6-hexamethyl-4-oxo-1-oxaspirohexane (**5**), and the minor product (13%) is tentatively assigned as 3,5,5-trimethyl-2-(1-hydroxy-1-methylethyl)cyclopent-2-enone (**6**).



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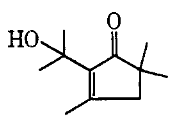

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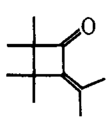
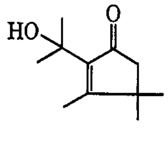


7

Compound **5** displays a strong band at 5.63 μ indicative of a cyclobutanone carbonyl,[4] and its 100-MHz nmr spectrum shows six different methyl groups. Confirmation of structure **5** was effected by alternate preparation from the *m*-chloroperbenzoic acid epoxidation of ketone **7**.[2]

The structure of compound **6** is assigned on the basis of its spectroscopic properties. The infrared spectrum of **6** displays carbonyl absorption (5.95 μ), a conjugated double bond (6.13 μ), and an alcohol group (2.92 μ). These data, along with ultraviolet absorption at 232 mμ, are in agreement with other examples of 2-cyclopentenones.[5] The nmr spectrum of **6** shows a two-proton quartet (J = 1.0 Hz) at τ 7.68 and a three-proton triplet (J = 1.0 Hz) at 7.83. The chemical shift of the olefinic methyl is as expected for a methyl β to the carbonyl group.[6] Possible alternate structures **8**, **9**, and **10** are therefore not compatible with the observed coupling patterns and chemical shifts.[7] The remainder of the spectrum shows six-proton singlets



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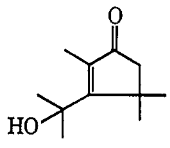

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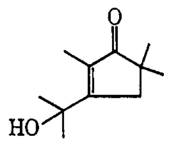

10

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[1] (a) Supported by Research Grant GP-6610 from the National Science Foundation. (b) National Institutes of Health Predoctoral Fellow 1966–1968.

[2] J. K. Crandall and D. R. Paulson, *J. Org. Chem.*, **33**, 991 (1968).

[3] See, for example, N. S. Crossley, A. C. Darby, H. B. Henbest, J. J. McCullough, B. Nicholls, and M. F. Stewart, *Tetrahedron Lett.*, 398 (1961), and references cited therein.

[4] R. T. Conley, "Infrared Spectroscopy,' Allyn and Bacon, Inc., Boston, Mass., 1966, p 141.

[5] A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," The Macmillan Co., New York, N. Y., 1966, p 66.

[6] The methyl resonance of 3-methylcyclopent-2-enone appears at τ 7.9.

[7] The methyl group in the 2 position of i appears at τ 8.30 while the methyl group in the 2 position of ii appears at τ 8.28: W. E. Doering, M. R. Wilcott, and M. Jones, *J. Amer. Chem. Soc.*, **84**, 1224 (1962).

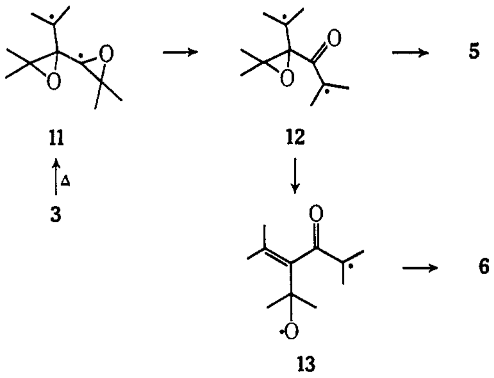
i

ii

at 8.65 [$C(CH_3)_2OH$] and 8.97 [$C(CH_3)_2CO$] in addition to a hydroxyl proton.

The pyrolytic rearrangement of diepoxide **3** can be described as shown in Chart I. This transformation is initiated by bond breakage in the more strained cyclopropyl ring which is followed by rearrangement of the epoxy radical moiety of **11** to α-keto radical **12**.[8] Radical coupling then gives epoxy ketone **5** directly. Subsequent rearrangement of **12** could give **13** which is probably the precursor of cyclopentenone **6**.[9]

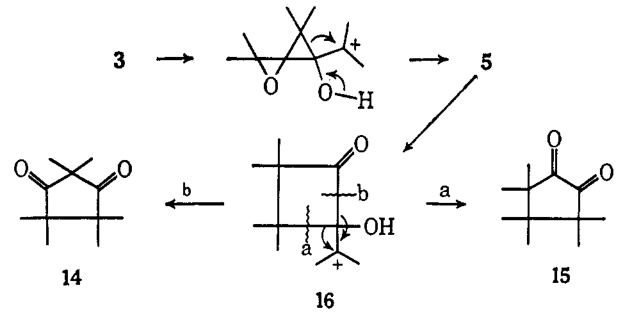
CHART I



Acid-catalyzed reaction of **3** in acetic acid containing sulfuric acid generated two new compounds in a 1:2 ratio. The minor component was identified as 2,2,4,4,5,5-hexamethylcyclopentane-1,3-dione (**14**) by its characteristic spectral properties.[10] The major material, an orange crystalline solid, is assigned as 3,3,4,4,5,5-hexamethylcyclopentane-1,2-dione (**15**). The nmr spectrum of **15** displays singlets at τ 9.05 and 8.86 in the ratio of 1:2, and the infrared spectrum shows a strong carbonyl at 5.72 μ with a characteristic overtone at 2.91 μ. Finally the ultraviolet spectrum displays weak absorption at 516 and 493 mμ. Taken together, these data clearly support the nonenolizable α-diketone structure **15**.[11] When epoxy ketone **5** was subjected to the conditions used in the acid-catalyzed rearrangement of **3**, compounds **14** and **15** were again obtained in a 1:2 ratio.

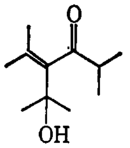
The acid-catalyzed transformations are visualized (Chart II) as involving protonation at one of the oxygen atoms, followed by bond heterolysis and preferential pinacolic migration to give **5**. Epoxy ketone **5**, which was not isolated from this reaction but which gave the same products under the reaction conditions, is most probably an intermediate species. Thus, protonation at the epoxy group and ring opening gives intermediate **16**. Pinacolic rearrangement of **16** by migration of bond a leads to **15** while acyl migration (bond b) leads to **14**.[12]

CHART II



The final aspect of the chemistry of **3** to be examined was its base-promoted transformation. Thus treatment of **3** with an ethereal solution of lithium diethylamide resulted in the formation of a mixture of two compounds. The relative ratio of these two products could be greatly varied by changing the reaction conditions. Treatment of this crude mixture with potassium hydroxide solution resulted in the formation of 2,5-dimethyl-4-isopropylidene-5-hydroxyhex-2-en-3-one (**17**) in good yield. The infrared spectrum of **17** shows hydroxyl absorption and a conjugated carbonyl at 6.04 μ. The nmr displays a six-proton singlet at τ 8.66 for the dimethylmethylol group, olefinic methyl singlets at 8.52 and 8.08, and an additional methyl on a double bond at 8.16 coupled weakly to the individual terminal methylene protons (4.20, 4.09), in addition to the hydroxyl proton. The ultraviolet spectrum displays a maximum at 218 mμ.[13] It was readily shown that **17** is one of the two products present in the diethylamide reaction product. When **3** was treated with lithium diethylamide containing an excess of diethylamine, the other compound noted above was obtained as the major product. This material is tentatively assigned as 1-(N,N-diethylamino)-2,5-dimethyl-4-isopropylidene-5-hydroxyhexan-3-one (**18**) on the basis of its spectral properties (see Experimental Section) and its conversion into **17** by aqueous base.

Attempted hydrogenation of **17** in methanol at atmospheric pressure was unsuccessful, but proceeded smoothly in methanolic hydroxide solution to give 2,5-dimethyl-4-isopropylidene-5-hydroxyhexan-3-one (**19**) in high yield. Treatment of **18** under the same conditions also gave **19** in high yield. The nmr spectrum (see Experimental Section) demonstrates that the isopropenyl group of **17** has been selectively saturated, while the infrared spectrum provides visible support for retention of the hydroxyl and conjugated carbonyl groups. Acid dehydration of keto alcohol **19** gave the known ketone **20**[2] in almost quantitative yield, thereby providing solid confirmation of the above assignments.



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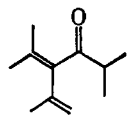

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The lithium diethylamide catalyzed rearrangement of **3** is interpreted as being initiated by β elimination[14] and subsequent ring opening as shown in Chart III.

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[8] T. J. Wallace and R. J. Gritter, *Tetrahedron*, **19**, 657 (1963).

[9] Precedent for the **12** → **13** conversion can be found in E. C. Sabatino and R. J. Gritter, *J. Org. Chem.*, **28**, 3437 (1963). A six-center intramolecular hydrogen abstraction followed by ring-closure completes the pathway to **6**.

[10] H. V. Hostettler, *Tetrahedron Lett.*, 1941 (1965).

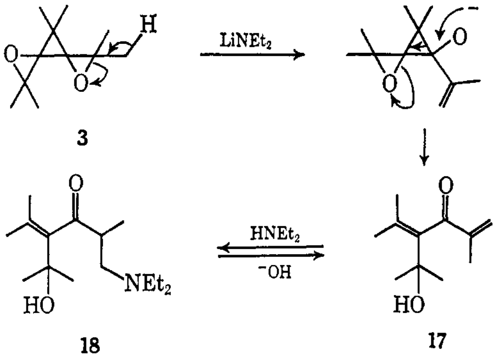
[11] N. J. Leonard and P. M. Mader, *J. Amer. Chem. Soc.*, **72**, 5388 (1950); R. S. Rasmussen, D. D. Tunnicliff, and R. R. Brattain, *ibid.*, **71**, 1068 (1949).

[12] Rearrangements of this type have been well studied. See for example: H. O. House and R. L. Wasson, *ibid.*, **79**, 1488 (1957).

[13] Other examples of highly substituted conjugated systems with anomalously low wavelength maxima are known. See, for example, W. F. Forbes, R. Shilton, and A. Balasubramanian, *J. Org. Chem.*, **29**, 3527 (1964); R. Criegee, U. Zirngibl, H. Furrer, D. Seebach, and G. Freund, *Chem. Ber.*, **97**, 2942 (1964).

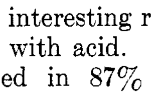
[14] J. K. Crandall and L. H. Chang, *J. Org. Chem.*, **32**, 435 (1967).

CHART III



Amino compound **18** is postulated as arising *via* Michael-type addition of diethylamine to the initial product **17**.

An interesting rearrangement occurs upon treatment of **17** with acid. A clean transformation product was isolated in 87% yield and identified as 2,4,4-trimethyl-5-isopropylidene-2-cyclopentenone (**21**). Again infrared bands at 5.92 and 6.16 μ are indicative of the cyclopentenone moiety.[6] This structure is supported by its nmr spectrum which shows a six-proton singlet at 8.72, a three-proton doublet (J = 1.5 Hz) at 8.28, three-proton singlets at 8.04 and 7.74, and a one-proton quartet (J = 1.5 Hz) at 3.39.[6] Confirmation of the five-membered ring structure proposed for the acid-catalyzed dehydration product **21** was secured by exhaustive hydrogenation. Three products were obtained from this treatment, two of which were collected as a mixture and shown to have a 5.77-μ carbonyl band as expected for a mixture of the epimeric saturated cyclopentanones **22**.[4] The remaining product is apparently the half-hydrogenated ketone **23** as determined from its spectroscopic properties (see Experimental Section). A possible formulation for this cyclization involves ionization of the hydroxyl group and cyclization of the resultant cation at the terminal methylene carbon.



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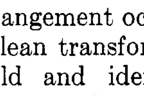

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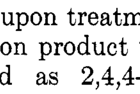

23

Experimental Section

General.—Infrared spectra were obtained with Perkin-Elmer Model 137 and 137-G infracord spectrophotometers and unless otherwise specified were taken in carbon tetrachloride solution. Nuclear magnetic resonance (nmr) spectra were obtained on Varian Associates A-60 and HR-100 spectrometers in carbon tetrachloride solution. Chemical shifts are given as τ values. Mass spectra were obtained with an AEI MS-9 mass spectrometer at 70 eV; ultraviolet spectra (uv) were taken on a Cary 14 spectrophotometer. Gas chromatography (glpc) was performed on Aerograph Model 600, Model 1200 (analytical, hydrogen flame detector), and A700 (preparative). Chromatographs and percentage composition data were estimated by peak areas (uncorrected). Melting points were determined in sealed capillary tubes. Anhydrous magnesium sulfate was used for all drying operations. Microanalyses were performed by Midwest Microlabs Inc., Indianapolis, Ind.

2,2,6,6,7,7-Hexamethyl-1,5-dioxadispiro[2.0.2.1]heptane (3).—To an ice-cold, mechanically stirred mixture of 1.80 g of **2** and 16.8 g of powdered, anhydrous sodium carbonate in 50 ml of methylene chloride was added dropwise 7.12 g of 40% peracetic acid which had been pretreated with a small amount of anhydrous sodium acetate. The mixture was stirred until the methylene chloride solution gave a negative test with moist starch–iodide paper. The solid salts were removed by suction filtration and washed well with additional solvent. The methylene chloride was removed from the filtrate by flash evaporation to give 2.17 g (95%) of **3** shown by glpc to contain only one significant component. Glpc collection gave pure **3**: ir (neat), 10.7 and 11.4 μ;[15] 100-MHz nmr, τ 8.86 (s, 6), 8.68 (s, 6) and 8.59 (s, 6). A precise mass spectrometric determination on the molecular ion of **3** gave m/e 182.1305 (calcd for $C_{11}H_{18}O_2$: 182.1307). Repeated attempts to obtain a satisfactory combustion analysis were unsuccessful.

Pyrolysis of 3.—A 100-mg sample of **3** was pyrolyzed in a flow system at 400° (0.25 mm)[2] to give 86 mg (86%) of a crude oil. Glpc analysis of this product showed two major compounds as 75 and 13% of the volatile material. No other component accounted for more than 2% of the mixture.

The major material was 2,2,4,4,5,5-hexamethyl-6-oxo-1-oxaspiro[2.3]hexane (**5**): ir, 5.63 (cyclobutanone)[4], 11.0, and 11.3 μ (epoxide);[15] 100-MHz nmr, τ 8.94 (s, 3), 8.89 (broad s, 6), 8.80 (s, 3), 8.65 (s, 3), and 8.59 (s, 3); uv max (hexane), 214 mμ (ϵ 865) and 336 (32).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.50; H, 10.02.

The minor product is assigned as 3,5,5-trimethyl-2-(1-hydroxy-1-methylethyl)cyclopent-2-enone (**6**): ir, 2.93, 5.92 and 6.14 μ; nmr, τ 8.97 (s, 6), 8.63 (s, 6), 7.83 (t, 3, J = 1 Hz), 7.68 (q, 2, J = 1 Hz), and 5.59 (s, 1); uv max (hexane), 232 mμ (ϵ 8750).

Acid-Catalyzed Rearrangement of 3.—To a solution of 1.5 g of **3** in 25 ml of glacial acetic acid was added a solution of 25 drops of concentrated sulfuric acid in 10 ml of glacial acetic acid. The resulting mixture was stirred at room temperature for 3 hr, poured into 100 ml of water, and extracted with five 25-ml portions of pentane. The pentane extracts were washed with two 25-ml portions of saturated sodium bicarbonate solution and dried. The solvent was removed by flash evaporation to give 1.3 g of crude product. Two compounds were isolated by glpc as 66 and 33% of the volatile reaction product.

The minor product is identified as 2,2,4,4,5,5-hexamethylcyclopentane-1,3-dione (**14**): ir, 5.80, 7.9, and 9.4 μ; nmr, τ 8.96 (s, 12) and 8.85 (s, 6); uv max (hexane), 215 mμ (ϵ 227) and 290 (27). These data agree in detail with those reported by Hostettler.[10]

The major product, an orange crystalline solid of mp 105–110°, is identified as 3,3,4,4,5,5-hexamethylcyclopentane-1,2-dione (**15**): ir, 2.91 (weak) and 5.75 μ; nmr, τ 9.05 (s, 6) and 8.86 (s, 12); uv max (hexane), 516 mμ (ϵ 25.5) and 493 (28.6).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.66; H, 10.04.

Acid-Catalyzed Rearrangement of 5.—A 45-mg sample of **5** was stirred with 15 ml of glacial acetic acid containing four drops of concentrated sulfuric acid for 4 hr, the mixture was poured into water and extracted with several portions of pentane. After drying the combined extracts, the solvent was removed to give a crude oil which was shown by glpc analysis to contain two components in the ratio of 1:2. Glpc isolation demonstrated that these were **14** and **15**, respectively.

2,2,4,4,5,5-Hexamethyl-6-oxo-1-oxaspiro[2,3]hexane(5).—To a solution of 100 mg of **7**[2] in 10 ml of methylene chloride was added 0.19 g of *m*-chloroperbenzoic acid and the resulting solution was refluxed for 6 days. The reaction mixture was washed with 10 ml of saturated sodium bicarbonate solution and dried. The methylene chloride was removed by flash evaporation to give 80 mg of crude **5**. Collection by glpc gave the major component (90%) which was identical with the material obtained from the pyrolysis of **3**.

Rearrangement of 3 by Lithium Diethylamide.—To a predried flask, cooled to 0°, and under a nitrogen atmosphere, was added 75 ml of anhydrous ether, 1.50 g of anhydrous diethylamine, and 12.2 ml of 1.6 N n-butyllithium solution in hexane. After stirring for 15 min, the ice bath was removed, 1.00 g of **3** was added, and the reaction mixture was heated to reflux for 12 hr. After pouring into 100 ml of water, the layers were separated and the aqueous layer was washed with three 50-ml portions of ether. The combined ethereal portions were washed with 100 ml of saturated sodium chloride solution and dried. The solvent was removed to give 0.95 g of a crude oil. Glpc analysis showed

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[15] Reference 4, p 130.

one major product as over 80% of the volatile reaction mixture, and nmr analysis of the crude material showed essentially the same spectrum as glpc-collected product. This was identified as 2,5-dimethyl-4-isopropylidene-5-hydroxyhex-2-en-3-one (**17**): uv max (hexane), 218 mμ (ϵ 6900), 262 (390), and 340 (11); ir, 2.84 (OH), 6.04 (conjugated carbonyl) and 10.6 μ; nmr, τ 8.66 (s, 6), 8.52 (s, 3), 8.16 (m, 3), 8.08 (s, 3), 4.20 (m, 1), and 4.09 (m, 1).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.25; H, 9.98.

When the above reaction was conducted at room temperature for 30 min or for 24 hr at reflux with an excess of diethylamine, a mixture of **17** and a new substance possessing a diethylamino function was obtained. This material was purified by extraction from ethereal solution with 1% hydrochloric acid solution followed by careful neutralization with saturated sodium bicarbonate solution to give a 60% yield of 1-(N,N-diethylamino)-2,5-dimethyl-4-isopropylidene-5-hydroxyhexan-3-one (**18**), the Michael addition product of diethylamine and **17**. Compound **18** displays the following spectral data: ir, 3.0, 5.92, 7.95, 8.4, 9.3, and 10.7 μ; 100 MHz nmr, τ 8.98 (d, 6, J = 6.1 Hz), 8.98 (t, 6, J = 6.6 Hz), 8.60 (s, 3), 8.51 (s, 3), 8.43 (s, 3), 8.24 (s, 3), 7.46 (apparent overlapping quartets, 4), 7.09 (m, 2), and 7.80 (m, 1). Examination of the nmr spectrum of the crude reaction product showed about a 6:1 ratio of **18** and **17**.

Stirring 100 mg of **18** in 25 ml of 20% potassium hydroxide solution for 2 hr followed by extraction with ether gave 45 mg (62%) of **17**.

Catalytic Hydrogenation of 17.—A solution of 0.30 g of **17** in 50 ml of 20% potassium hydroxide in methanol was hydrogenated at atmospheric pressure using 5% palladium-on-charcoal as catalyst. Exhaustive hydrogenation resulted in the uptake of 1 equiv of hydrogen. The resulting mixture was filtered to remove the catalyst, and the filtrate was poured into 100 ml of water and extracted several times with 25-ml portions of ether. The ethereal extracts were combined and dried, and the ether was removed to give 0.29 g (97%) of keto alcohol **19** which was further purified by glpc: ir, 2.95 (OH), 5.95 (conjugated carbonyl), and 6.10 μ (conjugated C=C); 100 MHz nmr, τ 8.95 (d, 6, J = 6.9 Hz), 8.55 (s, 6), 8.48 (s, 3), 8.21 (s, 3), 7.46 (s, 1), and 7.28 (septet, 1, J = 6.9 Hz).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.46; H, 10.95.

Catalytic Hydrogenation of 18.—Catalytic hydrogenation of 3.0 g of **18** in the same manner as the hydrogenation of **19** gave **14** in 85% yield.

Dehydration of 2,5-Dimethyl-4-isopropylidene-5-hydroxyhexan-3-one (19).—An 0.29-g sample of **19** was stirred in 25 ml of glacial acetic acid containing ten drops of concentrated sulfuric acid for 30 min. The reaction mixture was poured into 50 ml of water and extracted with three 25-ml portions of pentane. The combined pentane extracts were washed with 50 ml of saturated sodium bicarbonate solution and dried, and the pentane was removed to give 0.24 g of crude **20** which was purified by glpc and shown to be identical with an authentic sample.[2]

Acid-Catalyzed Rearrangement of 17.—The reaction was carried out on an 0.180-g sample in essentially the same manner as the acid-catalyzed rearrangement of **3**. The crude product (0.140 g) was shown by glpc to be 94% one compound. Glpc purification gave 2,4,4-trimethyl-5-isopropylidenecyclopent-2-enone (**21**): ir, 5.92 and 6.16 μ; nmr, τ 8.72 (s, 6), 8.28 (d, 3, J = 1.5 Hz), 8.04 (s, 3), 7.74 (s, 3) and 3.39 (s, 1, J = 1.5 Hz).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.36; H, 9.88.

Catalytic Hydrogenation of 21.—A solution of 140 mg of **21** in 50 ml of methanol was exhaustively hydrogenated at atmospheric pressure using 5% palladium-on-charcoal as catalyst. The reaction mixture was filtered to remove the catalyst, and the filtrate was poured into 100 ml of water and extracted several times with 50-ml portions of pentane. The pentane extracts were combined and dried, and the pentane was removed to give 120 mg of crude product. Glpc analysis showed three compounds as 63, 18, and 19% of the volatile reaction product. The 19% product was isolated by glpc collection and the other two products were collected together since they could not be effectively separated by preparation glpc.

The 19% product is tentatively assigned as 2,4,4-trimethyl-5-isopropylidenecyclopentanone (**23**) on the basis of the following spectroscopic evidence: ir, 5.85 and 6.16 μ; nmr, τ 8.98 (d, 3, J = 6.5 Hz), 8.77 (s, 3), 8.69 (s, 3), 8.09 (s, 3), and 7.82 (s, 3). The methylene and methine protons are obscured by the olefinic methyl resonances.

The other two products are assigned as the *cis* and *trans* isomers of 2,4,4-trimethyl-5-isopropylcyclopentanone (22): ir, 5.77 μ (strong, cyclopentanone).[4] The 100-MHz nmr spectrum of this mixture was very complicated in the methyl region as expected for a mixture of the two isomers of **18**.

Registry No.—**3**, 16980-16-8; **5**, 16980-17-9; **6**, 16980-18-0; **15**, 16980-19-1; **17**, 16980-20-4; **18**, 16980-21-5; **19**, 16980-22-6; **21**, 16980-23-7; **23**, 16980-24-8.

A One-Step Procedure for the Preparation of Tertiary α-Ketols from the Corresponding Ketones

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Steroidal ketones having a tertiary α-hydrogen react at −25° with oxygen and a trialkyl phosphite in the presence of a strong base to yield the corresponding α-ketols. The method is especially useful for the introduction of a 17α-hydroxyl group into 20-keto steroids, yields of 65% being obtained in many cases. The scope and limitations of the reaction are discussed.

The preparation of 17α-hydroperoxypregnan-20-ones and their reduction to the corresponding 17α-hydroxy compounds has been reported by Barton and coworkers.[2] The introduction of the 17α-hydroperoxy function was accomplished by treatment of the pregnan-20-one with oxygen in the presence of *t*-alkoxide in the corresponding *t*-alkyl alcohol, and, after isolation, the hydroperoxide was reduced to the alcohol, zinc dust in acetic acid being the preferred reagent.

Some years ago we employed this procedure to introduce a 17α-hydroxyl into compound **1** and obtained **2** in only 22% yield.[3] We encountered two difficulties in the conversion. Preparation of the hydroperoxide at ambient temperature, as advocated in the original procedure, gave yields of less than 50% on a 0.5-g scale, and on a 50 to 100 g scale none of the desired product could be isolated. Secondly, the yield of **2** (46%) on zinc dust reduction of the hydroperoxide was disappointing, and the product always contained traces of an impurity that was hard to

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